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Quantum nanostructures for plasmonics and high refractive index photonics

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Abstract

Although plasmonics and high refractive index photonics have experienced very fast growth thanks to classical physics concepts, there is an increasing interest in harnessing quantum physics concepts for further pushing the frontiers of these fields. In this context, this perspective highlights the importance of some quantum nanostructures for building nanomaterials and metamaterials with enhanced plasmonic and high refractive index properties. Two types of nanostructures displaying quantum properties are considered: (a) quantum confined nanostructures consisting of noble metals or standard semiconductors, (b) nanostructures built from alternative materials whose dielectric function and optical properties are driven by (possibly tailored) giant interband electronic transitions. A special emphasis is made on the potential of this latter type of nanostructures for achieving outstanding effects for applications, such as ultrabroadband light harvesting, giant refractive index, coupling between dielectric, low-loss plasmonic and magnetic properties, compositionally or externally tuneable optical response. Possible future developments to the field are discussed.

1. Introduction

Nanomaterials and metamaterials built from nanostructures supporting plasmon resonances or high refractive index resonances enable a strong light–matter interaction in subwavelength volumes, which is appealing for boosting the performance of applications in various fields such as energy, medicine, or optoelectronics. By suitably setting the nature, morphology, dimensions, and arrangement of the nanomaterial's or metamaterial's building blocks, the spectral, spatial, and energetic features of their resonances can be tuned to approach the requirements of the targeted application. In practice, the most suitable set of geometrical and compositional parameters is often found by calculations based on Maxwell equations. These calculations take into account the actual nanostructure morphology, dimensions, arrangement, and nature to determine, as a function of photon energy, quantities such as the near-field distribution or the power absorbed or scattered to the far-field. With such approach, the nature of the nanostructures is described by their energy dependent dielectric function ε (usually, taken equal to that of the corresponding bulk material), the values of which determine the type of resonances that can be achieved.

Plasmon resonances can be achieved in spectral regions where the real part of ε takes negative values ($\varepsilon_1 < 0$) [1, 2]. Such condition is fulfilled by noble metals (Au, Ag) in the visible and infrared, because of the dominant free-electron Drude susceptibility in these metals. Accordingly, plasmon resonances tuned in the visible and part of the infrared have been reported early in tailor-made noble metal nanostructures (nanospheres, nanorods, nanocylinders, nanostrips …). Plasmon resonances in such nanostructures can be achieved for dimensions down to 100 times smaller than the wavelength. They enable a strong near-field enhancement and/or a strong scattering to the far-field, which translate into a nano-antenna functionality useful for ultra-sensitive sensing or integrated nanoscale lighting. In addition, because of the non-zero imaginary part of ε for noble metals ($\varepsilon_2 > 0$), these resonances enable a strong optical absorption that is useful for efficient photothermal conversion. Note that, although such non-zero ε_2 implies a significant spectral width for the resonances of individual nanostructures, ultranarrow resonances needed for

ultra-sensitive sensing can be achieved, for instance, by assembling the nanostructures in periodic arrays to excite collective resonance modes.

High refractive index resonances, such as dielectric Mie resonances, can be achieved in spectral regions where the real part of ε takes high positive values ($\varepsilon_1 \gg 1$, equivalent to a high refractive index, $n > 3$–4) and its imaginary part ε_2 is small (equivalent to a small extinction coefficient k). Accordingly, such resonances tuned over the visible and infrared have been reported in semiconductor Si and Ge nanostructures that present a high n and a small k in these spectral regions ($n \sim 3.5$, $k < 0.1$) [3]. Such phenomena are based on optical interference within the nanostructure's volume so that their excitation requires larger dimensions than plasmon resonances, typically tens of times smaller than the wavelength, unless nanostructures with a much higher refractive index than Si or Ge can be found and used. It is worth noting that they can be achieved with fully transparent nanostructures ($\varepsilon_2 = 0$), so that they are useful for producing pure scatterers (with no absorption of light) for applications requiring low optical losses, e.g. displays.

Therefore, assembling tailor-made nanostructures supporting plasmon resonances or high refractive index resonances is a powerful approach to build nanomaterials or metamaterials with outstanding optical properties and functionalities. This approach has pushed the fast development of the fields of plasmonics and high refractive index photonics, with a recent focus on the search for nanostructures based on 'alternative' materials beyond Ag, Au, Si and Ge to enable enhanced plasmonic and high refractive index properties [4, 5]. Yet the growth of these fields has been strongly based on *classical physics concepts*. For example, the ε of the considered nanostructures is very often similar to that of the corresponding bulk materials. As another example, the search for plasmonic nanostructures based on alternative materials has mainly consisted in exploring ways to achieve a tuned free-electron Drude susceptibility through the density of such carriers: this is a classical physics-inspired approach. However, there is also an increasing number of demonstrations of nanomaterials and metamaterials built from *nanostructures harnessing quantum effects* to enable enhanced plasmonic or high refractive index properties. These demonstrations include *quantum confined nanostructures* whose ε is different from that of the corresponding bulk materials, and nanostructures based on *alternative materials whose ε and optical properties are driven by giant interband electronic transitions, even in their bulk state*. This perspective highlights works about such types of quantum nanostructures for plasmonics and high refractive index photonics, and points at possible future developments to the field. Note that there exist other types of quantum nanostructures (hybrid, plexcitronic, or graphene-based nanostructures) but they are not considered here.

2. Quantum confinement

2.1. Noble metal nanostructures

Quantum confinement in few-nm noble metal nanostructures may lead to an effective ε different from that of the bulk metal, because of a modified electronic band structure and of surface effects such as the free electron spill-out from the ionic core of the nanoparticle [1]. This latter effect, which is a consequence of the delocalized nature of free electrons, was also shown to lead to a weaker plasmonic near-field enhancement at the nanoscale vicinity of noble metal nanostructures when compared with classical physics expectations [6]. Quantum confinement is also relevant for ultrathin (few-nm) noble metal films, for which a markedly anisotropic ε has been predicted because of different electronic band structures in the in-plane and out-of-plane directions [7]. Quantum confinement is also crucial for nanogap quantum tunnelling plasmonic antennas [8, 9]. Such antennas consist of noble metal nanostructures separated by a nm-scale gap. By applying a voltage between these nanostructures, electrons can tunnel across the gap. Some of these electrons tunnel inelastically to generate photons. Such photon creation is stimulated by the plasmonic near-field in the gap, and the plasmonic response of the nanostructures can be optimized to ensure an efficient outcoupling of the created photons to the far-field. This has enabled designing nanoscale, electrically driven plasmonic light sources with a remarkable quantum efficiency above 10% [9]. Note that, besides quantum confinement, noble metal nanostructures have also been shown to enable other quantum phenomena when illuminated in the single photon regime. Some of such phenomena are two-plasmon interference [10], single-plasmon interference [11], or single-photon plasmonic coherent perfect absorption [12]. These phenomena, together with the demonstration of plasmonic light sources, are appealing for the design of integrated plasmonic elements for on-a-chip quantum information applications.

2.2. Si and Ge nanostructures

As it is the case for noble metal nanostructures, quantum confinement effects may become significant for Si and Ge nanostructures with a few-nm size [13, 14]. However, Si and Ge nanostructures that support high refractive index resonances such as the dielectric Mie ones present sizes ranging from several tens to several hundreds of nanometres, for which quantum confinement is not sizeable. Therefore, achieving

nanostructures presenting at the same time quantum confinement and high refractive index resonances requires alternative materials with a much higher refractive index (to achieve strong interference in smaller nanostructures) or with electronic properties with a stronger sensitivity to geometric confinement (to achieve quantum confinement in larger nanostructures). For that purpose, Bi could be considered, because bulk Bi presents a much higher refractive index than Si and Ge in the infrared ($n \sim 10$) and because quantum confinement has been observed in some Bi nanostructures with dimensions in the range of tens of nm [15].

3. Nanostructures based on giant interband materials

3.1. Tuning the electronic band structure to achieve a suitable ε

The search for alternative materials beyond Ag, Au, Si or Ge to produce nanostructures with enhanced plasmonic or high refractive index properties has focused many recent research efforts. Although this search may seem a pure metallurgy work, one must remind that it primarily aims at finding materials whose ε presents, possibly already in the bulk state, a suitable spectral dependence for achieving the targeted optical properties. Such spectral dependence should enable nanostructures to show in the required spectral region, for instance, plasmon resonances with lower losses than with noble metals (negative ε_1 together with a smaller ε_2) or high refractive index resonances with stronger confinement than with Si and Ge (higher ε_1 an n). Since the spectral dependence of the ε, n and k of materials are a direct consequence of their electronic band structure, harnessing quantum physics concepts to produce alternative materials with a suitably tailored energy band diagram appears to be an appealing way for achieving plasmonic or high refractive index nanomaterials and metamaterials with outstanding performance.

3.2. Giant interband materials

A clear example of how a suitably tailored electronic band structure leads to outstanding plasmonic and high refractive index properties is given by the class of 'giant interband materials' [16]. These materials display, already in their bulk form, giant interband electronic transitions (i.e. with a giant oscillator strength), which may occur for instance between parallel bands with a high electronic density of states and with many available electrons. These transitions lead to a giant absorption band in one region of the spectrum. Because of Kramers–Kronig relations, in a comparable way with the ultraviolet spectral features of Si [16–18], this results in negative values for the ε_1 of the material at higher energies. This also results in giant values of its ε_1 and n (much higher than those of Si and Ge) at smaller energies. This spectral dependence of ε makes giant interband materials excellent candidates for building nanostructures supporting plasmon resonances in the high energy region and strongly confined high refractive index resonances in the low energy region.

3.3. The example of Bi

Such spectral dependence and duality between plasmonic and giant refractive index resonances is evident in the case of the semi-metal Bi and its nanostructures. The ε of bulk Bi displays a giant interband absorption band at energies in the short-wave infrared around 0.8 eV and, consequently, a negative ε_1 in the ultraviolet and visible, and a giant ε_1 and n ($\varepsilon_1 \sim 100$, $n \sim 10$) in the mid-to-far infrared (figure 1(a)) [16, 17]. These outstanding spectral features have first enabled producing Bi nanoparticles showing plasmon resonances resulting in a broad and tuneable optical absorption in the ultraviolet and visible (figure 1(b)) [19]. It is worth noting that such absorption is likely purely due to the photoexcitation of electrons from one energy band to another, thus creating holes in the lower energy band (no free-carrier excitation) [17]. This implies that Bi nanoparticles combine ultraviolet–visible optical absorption properties typical of poor metal nanostructures with a photocarrier generation mechanism typical of semiconductors. This correlates with their efficient photocatalytic properties observed even under visible light excitation (see [17] and references therein for further details). Furthermore, thanks to the giant n (and small but sizeable k) of Bi in the mid-to-far infrared, resonant perfect absorption of light tuneable over this spectral region has been predicted and observed in Bi nanolayers more than 100 times thinner than the wavelength (figure 1(c)) [20]. More recently, the spectral dependence of the ε of Bi has been harnessed to design metamaterials enabling a broadband absorption of light [21–23]. In particular, self-assembled metamaterials consisting of a dense assembly of polydisperse Bi nanorods combining multiple plasmon resonances in the ultraviolet and visible with lossy dielectric Mie resonances (with $k \neq 0$) in the infrared have been produced to achieve an ultrabroadband absorption covering the whole solar spectrum together with mid infrared resonances useful for sensing [22, 23].

3.4. The example of Te

Bi is not the only giant interband material. For instance, the ε of the bulk semiconductor Te shows similar spectral features and therefore Te nanostructures present a similar duality between plasmon (in the
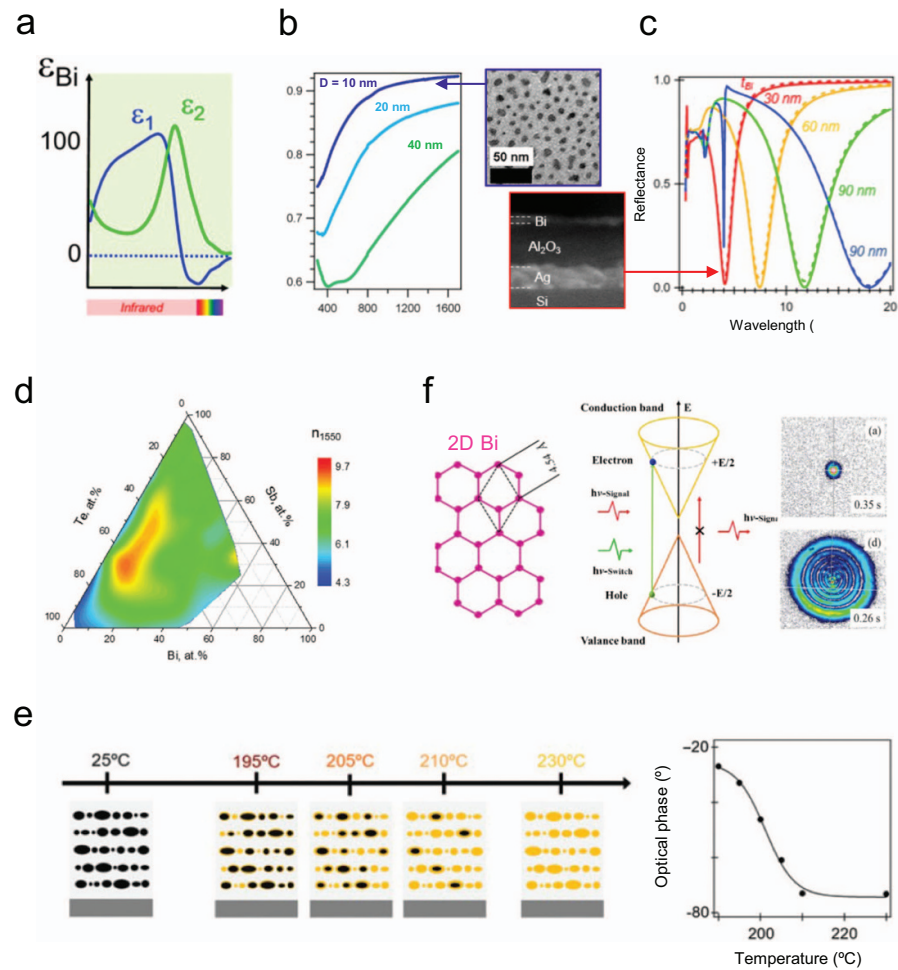
Figure 1. (a) Dielectric function ε of Bi as a function of energy from the far infrared to the ultraviolet. Reprinted with permission from [17]. Copyright 2017 American Chemical Society. (b) Plasmon resonances of Bi nanoparticles tunable over the ultraviolet and visible by adjusting the nanoparticle diameter D. Adapted with permission from [19]. Copyright 2012 American Chemical Society. (c) Perfect absorption at high refractive index resonances of Bi nanolayers tunable over the mid-to-far infrared by adjusting the nanolayer thickness t_{Bi}. Adapted with permission from [20]. Copyright 2018 Optical Society of America. (d) Refractive index at a wavelength of 1550 nm for ternary (Bi, Sb, Te) chalcogenides as a function of their stoichiometry. Reprinted with permission from [26]. Copyright 2019 Wiley VCH. (e) Temperature-controlled partial melting of Bi nanostructures (left panel) enabling the analog tuning of the optical phase reflected by a Bi-based metamaterial (right panel). Adapted with permission from [28]. Copyright 2020 Rosalia Serna, Johann Toudert *et al*, DeGruyter/Berlin/Boston, CCBY 4.0. (f) All-optical pump-probe switching of scattered light by 2D Bi nanostructures: atomic arrangement (left panel), electronic process (center panel) and scattering patterns (right panel) without (top) and with (bottom) pump light. Adapted with permission from [34]. Copyright 2017 American Chemical Society.

ultraviolet and visible) and lossy dielectric Mie resonances (in the visible, near and short-wave infrared). Thanks to this duality, polydisperse assemblies of Te nanoparticles strongly absorb light over the whole solar spectrum. Thanks to this absorbing character, together with their high thermal stability, these nanoparticles have been used to achieve efficient photothermal conversion for water desalinisation [24].

3.5. Giant interband materials: compositional tailoring of ε

An important characteristic of giant interband materials is the tunability of their electronic band structure and thus of their ε. Electronic band structure tuning has been reported by controlling the composition of ternary and quaternary (Bi, Sb, Te, Se) bulk chalcogenides, thus showing paths to achieve nanostructures with finely tuned plasmonic and giant refractive index properties (figure 1(d)) [25, 26]. Several of these compounds present a giant n in the infrared. Moreover, in contrast with Bi, some of them present a very low or zero k in this region. Such combined features have enabled the excitation of infrared circular surface displacement currents in Bi_2Te_3 slit-array metamaterials [27]. Considering that several (Bi, Sb, Te, Se) chalcogenides present topological insulator properties, this finding opens the way to a strong coupling of light with topological surface carriers, and therefore to connecting together on a single metamaterial platform high refractive index dielectric, low-loss plasmonic and magnetic/spin properties.

3.6. Giant interband materials: external tuning of ε

Beyond static compositional tailoring, the electronic band structure and ε of some giant interband materials has been shown to be tuneable in a dynamic way. This is the case of Bi and Ga, which present several known stable or metastable phases with different electronic band structures and ε: solid, amorphous and liquid for Bi [28], several solid phases, amorphous and liquid for Ga [29, 30]. Therefore, by varying the external temperature or heating up with laser pulses, Bi and Ga nanostructures can be switched from one phase to another to tune dynamically and reversibly their optical properties. Following this approach, an analog and reversible tuning of the optical properties of Bi-based metamaterials in a synapse-like fashion, interesting for switching and data storage applications, has been reported (figure 1(e)) [28]. Rich tuning capabilities are also expected for Ga nanostructures because of the polymorphism of this material. Also, because most of its phase transitions occur very close to room temperature, it is believed that such tuning can be achieved with a low energy consumption [30].

4. Possible future developments

4.1. Quantum confined metal nanostructures

Quantum confined metal nanostructures might be useful to produce broadband perfect absorbers with an ultrasmall footprint. Indeed, because of a more suitable spectral dependence of their ε, metal nanostructures small enough to display sizeable electronic confinement might be more prone to enabling broadband impedance matching in resonant cavity structures than nanostructures without such confinement [31].

4.2. Giant interband materials

The properties of nanostructures, nanomaterials and metamaterials based on the already known giant interband materials remain to be explored. In addition to its fundamental interest, this exploration is needed for the engineering and optimization of nanomaterials and metamaterials with outstanding plasmonic or high refractive index properties. Meanwhile, it should be noted that the known materials present an elemental (Bi, Te, Ga …) or simple compound nature (based on Bi, Sb, Te …). There are probably other compositions enabling better properties. Therefore, it will be interesting to design (bulk) materials on purpose with the help of electronic band structure calculations to achieve specific values of ε in specific spectral regions. Achieving a lower ε_2 (lower plasmonic losses), or a higher n and lower k in the desired spectral region, would of course be of interest. Among the design options, compositional, structural and defect engineering could be considered. The design could also aim at coupling a tailored ε spectrum with other specific properties, such as giant n and vanishing k in the mid or far infrared with topological surface conductivity (for low-loss magneto-optical applications), negative ε_1 toward the visible with surface reactivity (for energy applications), externally tuneable giant n in the visible (for applications in low-loss optoelectronics and photonics).

It will also be interesting to explore the properties of such alternative materials when grown as ultrathin structures toward the two-dimensional [32] and transdimensional regimes [33] for which quantum confinement might lead to a different electronic band structure and thus a different ε. For example, all-optical switching properties have been reported for two-dimensional Bi, in relation with its specific electronic band structure (figure 1(f)) [34]. Furthermore, the exploration of the two-dimensional and transdimensional regimes could lead to compounds whose optical properties could be sensitive to defects or strain and therefore be of interest for ultrasmall footprint switching and data storage applications.

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